

Water-emulsifiable isocyanates with improved properties

The invention relates to water-emulsifiable isocyanates 5 possessing improved emulsifiability and featuring increased hardness of coatings obtained using them, to processes for preparing them, and to their use.

Water-emulsifiable polyisocyanates are added as crosslinking 10 agents to aqueous polymer dispersions and have been widely described in the literature. Emulsifiability in water is brought about by blending the polyisocyanates with emulsifiers which are obtained by reacting the polyisocyanates with hydrophilic molecules.

15 Hydrophilic molecules commonly used include nonionic hydrophilic molecules such as polyalkylene oxide alcohols.

EP-A2 206 059 describes water-dispersible polyisocyanate 20 formulations comprising an aliphatic polyisocyanate and a reaction product of an aliphatic polyisocyanate with a monohydric or polyhydric, nonionic polyalkylene ether alcohol emulsifier which has at least one polyether chain containing at least 10 ethylene oxide units. As suitable polyisocyanates, extensive 25 lists are given of aliphatic and cycloaliphatic diisocyanates, more preferably isocyanurates and biurets based on 1,6-diisocyanatohexane (HDI) and/or isocyanurates based on 1-isocyanato-3,5,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI).

30 EP-A1 540 985 likewise describes polyisocyanate mixtures, but in this case the polyether chains have an average ethylene oxide unit content of from 5.0 to 9.9.

35 EP-A2 486 881 describes nonaqueous aliphatic polyisocyanate formulations comprising polyisocyanates from a list of aliphatic polyisocyanates and comprising an amount, sufficient to ensure the dispersibility of the aliphatic polyisocyanate, of a reaction 40 product of an aromatic or aliphatic diisocyanate and a monohydric or polyhydric polyalkylene ether alcohol having at least 8 ethylene oxide units in the polyether chain.

DE-A1 199 58 170 describes polyether-modified, water-dispersible polyisocyanate mixtures which have been modified with monohydric 45 polyalkylene oxide polyether alcohols. Very particular preference is given to polyisocyanates or polyisocyanate mixtures with an

isocyanurate structure based on HDI, IPDI and/or
4,4'-diisocyanatodicyclohexylmethane.

DE-A1 198 22 890 describes aqueous two-component polyurethane
5 coating systems whose hardener component is prepared from
polyalkylene oxide polyether alcohols and aliphatically and/or
cycloaliphatically attached isocyanate groups, preferably
isocyanurate structures based on HDI, IPDI and/or
4,4'-diisocyanatodicyclohexylmethane, under allophanatization
10 conditions. The predominant attachment of polyether chains by way
of allophanate groups is also known from DE-A1 198 47 077.

Nonionic emulsifiers described include
polyvinylpyrrolidone-modified polyisocyanates (EP-A2 754 713).

15 Also in use as actively dispersing units are polyalkylene oxide
ethers containing carboxylic acid groups, as described in
DE-A1 100 07 820 and DE-A1 41 13 160, or polyether ester alcohols
(EP-A1 728 785).

20 DE-A1 40 01 783 describes polyisocyanate mixtures which, with a
uretdione content of 1 to 23% by weight, contain chemically
bonded carboxyl groups for dispersibility.

25 Furthermore, carboxyl-containing compounds are described as
emulsifiers (EP-A2 548 669), tertiary amino and/or ammonium
groups (EP-A1 582 166 and EP-A1 531 820), acidic esters of
phosphoric acid (DE-A1 197 24 199) or sulfonic acids
(EP-A1 703 255).

30 A disadvantage of the polyisocyanate mixtures described is that
they do not meet the requirements imposed on the hardness of the
coatings obtainable using them.

35 Water-emulsifiable isocyanates can be dissolved in organic
solvents such as, for example, carbonic esters or lactones for
the purpose of improving dispersibility, as described in
EP-A 697 424.

40 From "Lackharze" [Resins for Coatings] (edited by D. Stoye and W.
Freitag, Hanser 1996, p. 195) it is known that IPDI trimer, which
gives resins for coatings a comparatively high level of hardness,
even going as far as brittleness, is frequently employed in
blends with HDI derivatives in order to lessen the hardness.

Users require the water-emulsifiable isocyanates to have the following properties:

1. The isocyanate should be easy to emulsify; having to use demanding apparatus such as high-shear stirring elements is deprecated.
2. The emulsion should be fine, since otherwise the gloss may be disrupted or turbidity may appear, for example.
3. In the case of coatings, a frequent desire is for a high ultimate hardness.
4. The ultimate hardness should be attained as quickly as possible.

It is an object of the present invention to provide water-emulsifiable polyisocyanates which exhibit improved emulsifiability properties and with which it is possible to produce coatings having high hardness, rapid increase in hardness, and enhanced emulsifiability at the same time.

We have found that this object is achieved by mixtures comprising

(A) an isocyanurate and/or biuret of 1,6-diisocyanatohexane (HDI),

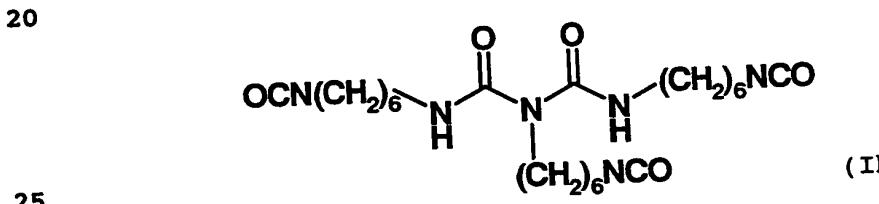
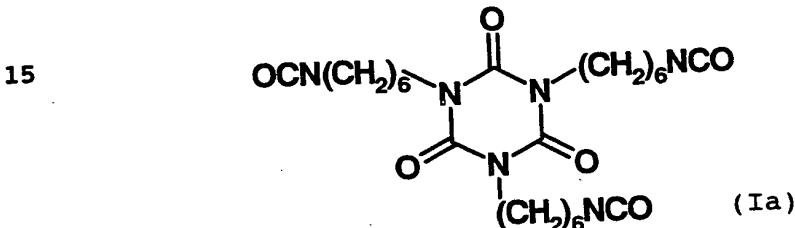
(B) an isocyanurate of
1-isocyanato-3,5,5-trimethyl-5-isocyanatomethylcyclohexane
(IPDI),

(C) at least one emulsifier, obtainable by reacting at least one diisocyanate (C2) selected from tetramethylene diisocyanate, hexamethylene diisocyanate (HDI), dodecamethylene diisocyanate, 1,4-diisocyanatocyclohexane,
4,4'-di(isocyanatocyclohexyl)methane, trimethylhexane diisocyanate, tetramethylhexane diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-(isocyanatomethyl)cyclohexane (IPDI), 2,4- or 2,6-tolylene diisocyanate and the isomer mixtures thereof, tetramethylxylylene diisocyanate, p-xylylene diisocyanate, 2,4'- or 4,4'-diisocyanatodiphenylmethane with at least one component (C1) containing at least one group which is reactive toward isocyanate groups and containing at least one hydrophilic group, and

(D) if desired, solvent.

The mixtures of the invention prove readily emulsifiable, lead to a fine, stable emulsion, and can be used to give coatings which exhibit a rapid increase in hardness and a high ultimate hardness.

5 Polyisocyanates (A) are isocyanurates (A1) and/or biurets (A2) of 1,6-diisocyanatohexane (HDI). In accordance with the invention this includes those polyisocyanates composed to an extent of at least 50% by weight, preferably at least 66%, more preferably at least 75%, very preferably at least 85%, and in particular at least 95% by weight, of compounds of the formula (Ia) and/or (Ib),



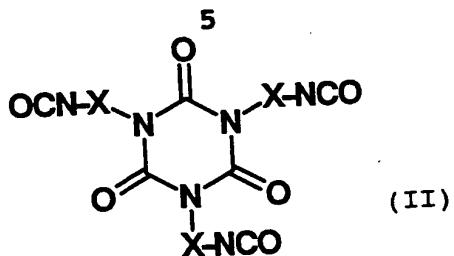
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and their higher homologues.

The composition of the polyisocyanates, i.e., for example, the fractions of isocyanurates and/or biurets and their higher homologues, and the average functionality are determined in this specification by gel permeation chromatography using polystyrene as standard and tetrahydrofuran as eluent.

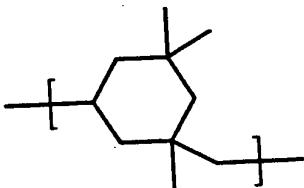
35 Polyisocyanates (B) are isocyanurates of 1-isocyanato-3,5,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI). In accordance with the invention, this includes those polyisocyanates which are composed to an extent of at least 50% by weight, preferably at least 66%, more preferably at least 75%, very preferably at least 85%, and in particular at least 95% by weight, of the compound of the formula (II),

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in which X is

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and their higher homologues.

Suitable emulsifiers (C) in accordance with the invention are
20 compounds obtainable by reacting at least one diisocyanate (C2)
with at least one, preferably 1 to 2, particularly preferably one
component (C1) containing at least one group which is reactive
toward isocyanate groups and containing at least one hydrophilic
group. (C1) is referred to below as "hydrophile".

25 Examples of isocyanate-reactive groups are hydroxyl groups (-OH),
unsubstituted or monosubstituted amino groups or mercapto groups
(-SH), preferably hydroxyl groups.

30 Generally, therefore, the emulsifiers (C) contain component (C1)
in chemically attached form.

The components (C1) may, for example, comprise compounds such as
are known in the prior art: for example, from the prior art cited
35 in the introduction.

In particular, these may be compounds which contain at least one
isocyanate-reactive group and

- 40 - (Cl_a) at least one cationic hydrophilic group,
- (Cl_b) at least one anionic hydrophilic group or
- (Cl_c) at least one nonionic hydrophilic group.

45 Preferred compounds (C1) contain 1 to 3 isocyanate-reactive
groups and 1 to 3 hydrophilic groups, more preferably 1 to 2
isocyanate-reactive groups and 1 to 2 hydrophilic groups, and

very preferably one isocyanate-reactive group and one hydrophilic group.

Compounds (Cl_a) contain at least one isocyanate-reactive group
5 and at least one cationic hydrophilic group or at least one hydrophilic group which can be converted into a cationic group, and are, for example, compounds such as those described in EP-A1 582 166, especially from page 5 line 42 to page 8 line 22 and in particular from page 9 line 19 to page 15 line 34 therein,
10 or in EP-A1 531 820, especially from page 3 line 21 to page 4 line 57 therein, or in DE-A1 42 03 510, especially from page 3 line 49 to page 5 line 35 therein. Those documents are explicitly incorporated into the present disclosure content by reference.

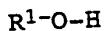
15 Compounds (Cl_b) contain at least one isocyanate-reactive group and at least one anionic hydrophilic group or at least one hydrophilic group which can be converted into an anionic group, and are, for example, compounds as described in EP-A1 703 255, especially from page 3 line 54 to page 4 line 38 therein, in
20 DE-A1 197 24 199, especially on page 3 lines 4 to 30 therein, in DE-A1 40 10 783, especially column 3 lines 3 to 40 therein, in DE-A1 41 13 160, especially from column 3 line 63 to column 4 line 4 therein, and in EP-A2 548 669, especially from page 4 line 50 to page 5 line 6 therein. Those documents are expressly hereby
25 incorporated into the present disclosure content by reference.

Compounds (Cl_c) contain at least one isocyanate-reactive group and at least one nonionic hydrophilic group and are for example compounds as described in EP-A2 754 713, especially on page 3
30 lines 31 to 51 therein, in EP-A2 206 059, especially on page 8 line 33 to page 9 line 26 therein, in EP-A2 486 881, especially on page 2 lines 42 to 54 therein, in EP-A1 540 985, especially on page 4 lines 43 to 58 therein, in EP-A1 728 785, especially on page 4 line 55 to page 5 line 54 therein, in EP-A1 959 115, especially on page 4 lines 23 to 46 therein, in DE-A1 199 58 170, especially on page 4 lines 22 to 48 therein, and in DE-A1 100 07 820, especially from page 4 line 10 to page 5 line 12 therein. Those documents are hereby expressly incorporated into the present disclosure content by reference.

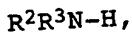
40 The hydrophiles (C1) are preferably compounds (Cl_c) containing at least one isocyanate-reactive group and at least one nonionic hydrophilic group.

Particularly preferred hydrophiles (Clc) are polyalkylene oxide polyether alcohols obtainable by alkoxylating suitable initiator molecules.

5 Suitable initiator molecules for the preparation of monohydric polyalkylene oxide polyether alcohols are thiol compounds, monohydroxy compounds of the formula



10 or secondary monoamines of the formula



15 in which R^1 , R^2 , and R^3 independently of one another are each C_1-C_{18} alkyl, C_2-C_{18} alkyl uninterrupted or interrupted by one or more oxygen and/or sulfur atoms and/or by one or more substituted or unsubstituted imino groups, or are C_6-C_{12} aryl, C_5-C_{12} cycloalkyl 20 or a five- or six-membered heterocycle containing oxygen, nitrogen and/or sulfur atoms, or R^2 and R^3 together form an unsaturated, saturated or aromatic ring whose members are uninterrupted or interrupted by one or more oxygen and/or sulfur atoms and/or by one or more substituted or unsubstituted imino 25 groups, it being possible for the radicals mentioned each to be substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles.

Preferably R^1 is C_1 to C_4 alkyl, i.e., methyl, ethyl, iso-propyl, 30 n-propyl, n-butyl, iso-butyl, sec-butyl or tert-butyl; very preferably R^1 is methyl.

Examples of suitable monofunctional initiator molecules may be saturated monoalcohols such as methanol, ethanol, n-propanol, 35 isopropanol, n-butanol, isobutanol, sec-butanol, the isomeric pentanols, hexanols, octanols and nonanols, n-decanol, n-dodecanol, n-tetradecanol, n-hexadecanol, n-octadecanol, cyclohexanol, cyclopentanol, the isomeric methylcyclohexanols or hydroxymethylcyclohexane, 3-ethyl-3-hydroxymethyloxetane, or 40 tetrahydrofurfuryl alcohol; unsaturated alcohols such as allyl alcohol, 1,1-dimethylallyl alcohol or oleyl alcohol, aromatic alcohols such as phenol, the isomeric cresols or methoxyphenols, araliphatic alcohols such as benzyl alcohol, anisyl alcohol or cinnamyl alcohol; secondary monoamines such as dimethylamine, 45 diethylamine, dipropylamine, diisopropylamine, di-n-butylamine, diisobutylamine, bis(2-ethylhexyl)amine, N-methyl- and N-ethylcyclohexylamine or dicyclohexylamine, heterocyclic

secondary amines such as morpholine, pyrrolidine, piperidine or 1H-pyrazole, and also amino alcohols such as 2-dimethylaminoethanol, 2-diethylaminoethanol, 2-diisopropylaminoethanol, 2-dibutylaminoethanol, 5 3-(dimethylamino)-1-propanol or 1-(dimethylamino)-2-propanol.

Alkylene oxides suitable for the alkoxylation reaction are ethylene oxide, propylene oxide, iso-butylene oxide, vinyloxirane and/or styrene oxide, which may be used in any order or else in a 10 mixture in the alkoxylation reaction.

Preferred alkylene oxides are ethylene oxide, propylene oxide, and mixtures thereof; particular preference is given to ethylene oxide.

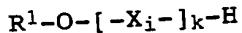
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Preferred compounds (Clc) are polyether alcohols based on polyalkylene oxide polyether alcohols prepared using saturated aliphatic or cycloaliphatic alcohols of the abovementioned type as initiator molecules. Very particular preference is given to 20 those based on polyalkylene oxide polyether alcohols prepared using saturated aliphatic alcohols having 1 to 4 carbon atoms in the alkyl radical. Polyalkylene oxide polyether alcohols prepared starting from methanol are especially preferred.

25 The monohydric polyalkylene oxide polyether alcohols contain on average generally from 5 to 35, preferably from 7 to 30, more preferably from 7 to 25, very preferably from 10 to 22, alkylene oxide units per molecule, in particular from 10 to 22 ethylene oxide units.

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Preferred polyether alcohols (Clc) are, therefore, compounds of the formula



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where

R^1 is as defined above,

k is an integer from 5 to 35, preferably from 7 to 30, more 40 preferably from 7 to 25, and in particular from 10 to 22, and each X_i can be selected, independently of one another for $i = 1$ to k, from the group consisting of $-CH_2-CH_2-O-$, $-CH_2-CH(CH_3)-O-$, $-CH(CH_3)-CH_2-O-$, $-CH_2-C(CH_3)_2-O-$, $-C(CH_3)_2-CH_2-O-$, $-CH_2-CHVin-O-$, $-CHVin-CH_2-O-$, $-CH_2-CHPh-O-$ and $-CHPh-CH_2-O-$, preferably from the 45 group consisting of $-CH_2-CH_2-O-$, $-CH_2-CH(CH_3)-O-$ and

$-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-$, and more preferably $-\text{CH}_2-\text{CH}_2-\text{O}-$
where Ph is phenyl and Vin is vinyl.

The polyether alcohols may further contain, as hydrophilic
5 synthesis components, minor amounts of other isocyanate-reactive
compounds containing anionic or cationic groups - for example,
with carboxylate, sulfonate or ammonium groups. This, however, is
less preferred.

10 Diisocyanates (C2) are selected in accordance with the invention
from the group consisting of tetramethylene diisocyanate,
hexamethylene diisocyanate, dodecamethylene diisocyanate,
1,4-diisocyanatocyclohexane, 4,4'-di(isocyanatocyclo-
hexyl)methane, trimethylhexane diisocyanate, tetramethylhexane
15 diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-(isocyanato-
methyl)cyclohexane, 2,4- or 2,6-tolylene diisocyanate and the
isomer mixtures thereof, tetramethylxylylene diisocyanate,
p-xylylene diisocyanate, 2,4'- or 4,4'-diisocyanatodiphenyl-
methane, and also a mixture of at least two of these
20 diisocyanates. Preferably, however, one of these components or an
isomer mixture is reacted.

Particular preference is given to hexamethylene diisocyanate,
4,4'-di(isocyanatocyclohexyl)methane, 1-isocyanato-3,3,5-tri-
25 methyl-5-(isocyanatomethyl)cyclohexane, tetramethylxylylene
diisocyanate, 2,4'- or 4,4'-diisocyanatodiphenylmethane and 2,4-
or 2,6-tolylene diisocyanate and the isomer mixtures thereof,
very particular preference to hexamethylene diisocyanate,
1-isocyanato-3,3,5-trimethyl-5-(isocyanatomethyl)cyclohexane and
30 2,4- or 2,6-tolylene diisocyanate, and especially 2,4- or
2,6-tolylene diisocyanate and the isomer mixtures thereof.

The diisocyanates are generally present to the extent of at least
75 mol% as monomers, preferably to the extent of at least
35 85 mol%, more preferably at least 90 mol%, and, with very
particular preference, at least 95 mol%.

To react the diisocyanates (C2) with the isocyanate-reactive
compounds (C1) it is normal to use from 60 to 120 mol%,
40 preferably from 80 to 120 mol%, more preferably from 90 to
110 mol%, and in particular from 100 mol% of isocyanate-reactive
groups in (C1) per mole of isocyanate groups in (C2).

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To prepare the component which is active as emulsifier (C) the starting components (C1) and (C2) are reacted with one another at temperatures from 40 to 180°C, preferably 50 to 150°C, observing the specified molar ratio.

5 The reaction time is generally 10 min to 5 hours, preferably 15 min to 4 hours, more preferably 20 to 180 min, and very preferably 30 to 120 min.

10 In order to accelerate the reaction it is possible where appropriate to use suitable catalysts.

These are the customary catalysts which are known for these purposes, examples being metal carboxylates, metal chelates or 15 tertiary amines of the type described in GB-A-0 994 890, alkylating agents of the type described in US-A-3 769 318, or strong acids as described by way of example in EP-A-0 000 194.

Suitable catalysts are, in particular, zinc compounds, such as 20 zinc(II) stearate, zinc(II) n-octanoate, zinc(II) 2-ethyl-1-hexanoate, zinc(II) naphthenate or zinc(II) acetylacetone, tin compounds, such as tin(II) n-octanoate, tin(II) 2-ethyl-1-hexanoate, tin(II) laurate, dibutyltin oxide, dibutyltin dichloride, dibutyltin diacetate, dibutyltin 25 dilaurate, dibutyltin dimaleate or dioctyltin diacetate, aluminum tri(ethyl acetoacetate), iron(III) chloride, potassium octoate, manganese compounds, cobalt compounds or nickel compounds, and strong acids, such as trifluoroacetic acid, sulfuric acid, hydrogen chloride, hydrogen bromide, phosphoric acid or 30 perchloric acid, for example, or any desired mixtures of these catalysts.

Suitable though less preferred catalysts for the process are also those catalysts as described for example in EP-A-0 649 866 on 35 page 4 line 7 to page 5 line 15.

Preferred catalysts for the process of the invention are zinc compounds of the abovementioned type. Very particular preference is given to using zinc(II) n-octanoate, zinc(II) 40 2-ethyl-1-hexanoate and/or zinc(II) stearate.

Where used, these catalysts are employed in an amount of from 0.001 to 5% by weight, preferably 0.005 to 1% by weight, based on the overall weight of the reactants.

The polyaddition reaction for preparing the polyurethane formulation of the invention may take place with particular preference in the presence of cesium salts, as described in the earlier German patent application of December 12, 2001 bearing reference 10161156.0. Preferred cesium salts are compounds in which the following anions are employed: F⁻, Cl⁻, ClO⁻, ClO₃⁻, ClO₄⁻, Br⁻, I⁻, IO₃⁻, CN⁻, OCN⁻, NO₂⁻, NO₃⁻, HCO₃⁻, CO₃²⁻, S²⁻, SH⁻, HSO₃⁻, SO₃²⁻, HSO₄⁻, SO₄²⁻, S₂O₂²⁻, S₂O₄²⁻, S₂O₅²⁻, S₂O₆²⁻, S₂O₇²⁻, S₂O₈²⁻, H₂PO₂⁻, H₂PO₄⁻, HPO₄²⁻, PO₄³⁻, P₂O₇⁴⁻, (OC_nH_{2n+1})⁻, 10 (C_nH_{2n-1}O₂)⁻, (C_nH_{2n-3}O₂)⁻, and (C_{n+1}H_{2n-2}O₄)²⁻, n standing for numbers from 1 to 20.

Particularly preferred compounds are cesium carboxylates in which the anion is of the formula (C_nH_{2n-1}O₂)⁻ or (C_{n+1}H_{2n-2}O₄)²⁻ where n is from 1 to 20. Especially preferred cesium salts contain 15 monocarboxylate anions of the formula (C_nH_{2n-1}O₂)⁻ where n stands for numbers from 1 to 20. Particular mention may be made here of formate, acetate, propionate, hexanoate, and 2-ethylhexanoate.

20 The cesium salts are used in amounts of from 0.01 to 10 mmol of cesium salt per kg of solvent-free reaction mixture. They are preferably used in amounts of from 0.05 to 2 mmol of cesium salt per kg of solvent-free reaction mixture.

25 The cesium salts can be added to the reaction mixture in solid form, but preferably in dissolved form. Suitable solvents are polar, aprotic solvents or else protic solvents. Particularly suitable besides water are alcohols; especially suitable are polyols, such as are also used as synthesis units for 30 polyurethanes, such as ethane-, propane-, and butane-diols, for example. The use of the cesium salts makes it possible to carry out the polyaddition reaction under the customary conditions.

Addition to the reaction mixture may take place by any desired 35 method. Thus, for example, it is possible to admix the catalyst (where used) either to the polyisocyanate component (A), (B), (C₂) and/or to the emulsifier component (C₁) before the beginning of the actual reaction. It is also possible to add the catalyst to the reaction mixture at any time during the reaction or else, 40 in a two-stage reaction regime, following the urethanization, i.e., when the NCO content corresponding theoretically to complete conversion of isocyanate and hydroxyl groups has been reached.

45 The sequence in which components (A), (B), and (C) are mixed is not critical to the invention: for example, the components may be mixed with one another simultaneously, (C), or at least part of

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it, can be included in an initial charge and then (A) and/or (B) added to that initial charge, or (A) or (B), at least in part, can be included in an initial charge, (C) can be added, and then the last component can be added.

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The course of the reaction can be monitored by determining the NCO content by means, for example, of titrimetry. When the target NCO content has been reached the reaction is terminated. In the case of a purely thermal reaction regime, this can be done, for example, by cooling the reaction mixture to room temperature.

10 example, by cooling the reaction mixture to room temperature. Where a catalyst of the aforementioned type is used, however, the reaction is generally stopped by adding suitable deactivators. Examples of suitable deactivators include organic or inorganic acids, the corresponding acid halides, and alkylating agents.

15 Examples that may be mentioned include phosphoric acid, monochloroacetic acid, dodecylbenzenesulfonic acid, benzoyl chloride, dimethyl sulfate, and, preferably, dibutyl phosphate and also di-2-ethylhexyl phosphate. The deactivators can be used in amounts of from 1 to 200 mol%, preferably from 20 to 100 mol%, based on the number of moles of catalyst.

20 The resultant polyisocyanate mixtures generally have an NCO content of preferably 6.0 to 23.0% by weight, more preferably 8.5 to 22.0% by weight.

25

The resulting polyisocyanate mixtures generally have a viscosity at 23°C of preferably 0.2 to 20 Pas, more preferably 0.5 to 8 Pas.

25 The process may be carried out where appropriate in a suitable solvent (D) which is inert toward isocyanate groups. Examples of 30 suitable solvents are the conventional paint solvents known per se, such as ethyl acetate, butyl acetate, ethylene glycol monomethyl or monoethyl ether acetate, 1-methoxy-2-propyl acetate, 3-methoxy-n-butyl acetate, acetone, 2-butanone, 35 iso-butyl methyl ketone, 4-methyl-2-pentanone, cyclohexanone, cyclopentanone, toluene, xylene, chlorobenzene, white spirit, aromatics with relatively high degrees of substitution, such as are sold, for example, under the names Solventnaphtha®, Solvesso®, Shellsol®, Isopar®, Nappar® and Diasol®, propylene glycol diacetate, diethylene glycol dimethyl ether, dipropylene glycol dimethyl ether, diethylene glycol ethyl and butyl ether acetate, N-methylpyrrolidone, and N-methylcaprolactam, and also, preferably, carbonic esters or lactones, which are specified in EP-A1 697 424, page 4 lines 4 to 32, more preferably dimethyl carbonate, diethyl carbonate, 1,2-ethylene carbonate and 45 1,2-propylene carbonate, lactones such as β -propiolactone,

γ -butyrolactone, ϵ -caprolactone, and ϵ -methylcaprolactone, or else any desired mixtures of such solvents.

It is also possible first to prepare the isocyanates of the 5 invention without solvent and then to use a solvent (D) to take up the product thus obtainable.

The mixtures of the invention preferably comprise in solvent-free form

- 10 (A) 30 - 90%, preferably 50 to 90%, by weight,
(B) 5 - 60%, preferably 5 - 50%, by weight, and
(C) 5 - 40%, preferably 5 - 50%, by weight,

15 the sum of (A), (B), and (C) making 100% by weight.

Based on the total mixture, the solvent (D) may be present in amounts of from 0 to 60% by weight, preferably in amounts of from 0 to 50% by weight.

20 The mixtures of the invention may be dispersed preferably in water for the purpose of preparing aqueous dispersions; with particular preference, the mixtures of the invention are mixed into aqueous dispersions.

25 The polyisocyanate formulation of the invention is suitable for modifying aqueous coating materials (paints, protective coatings) for substrates such as wood, wood veneer, paper, paperboard, cardboard, textile, leather, nonwoven, plastics surfaces, glass, 30 ceramic, mineral building materials such as cement moldings and fiber cement slabs, coated or uncoated metals, adhesives or impregnating compositions, for dyeing, for example, based on aqueous dispersions or solutions with a solids content of from 5 to 40% by weight, preferably from 5 to 20% by weight. Suitable 35 coating materials include the aqueous dispersions, known per se, of homopolymers and copolymers of olefinically unsaturated monomers or polyurethanes or else solutions of natural substances, such as of casein, for example.

40 The polyisocyanate formulations of the invention are added to the aqueous coating materials generally in an amount of 1 to 25% by weight, preferably from 2.5 to 20% by weight, based on the solids content of the coating material.

45 They are applied to the substrate in a known manner by means, for example, of spraying at a rate of from 5 to 50 g solids/m².

Suitable dispersions of homopolymers or copolymers of olefinically unsaturated monomers are, for example, conventional dispersions of homopolymers or copolymers based on vinyl esters of carboxylic acids having 2 to 18, preferably 2 to 4, carbon atoms such as vinyl acetate in particular, where appropriate with up to 70% by weight, based on the total amount of olefinically unsaturated monomers, of other olefinically unsaturated monomers, and/or of homopolymers or copolymers of (meth)acrylic esters of alcohols having 1 to 18, preferably 1 to 4, carbon atoms, such as (meth)acrylic acid, methyl, ethyl, propyl, hydroxyethyl or hydroxypropyl esters in particular, together where appropriate with up to 70% by weight of other olefinically unsaturated monomers, and/or butadiene-styrene copolymers having a butadiene content of about 20 to 60% by weight, and/or of other diene polymers or copolymers such as polybutadiene or copolymers of butadiene with other olefinically unsaturated monomers such as styrene, acrylonitrile and/or methacrylonitrile, for example, and/or aqueous dispersions of polymers or copolymers of 2-chloro-1,3-butadiene, where appropriate with other olefinically unsaturated monomers of the type exemplified above, e.g., those with a chlorine content of about 30 to 40% by weight, in particular a chlorine content of about 36% by weight.

Preference is given to aqueous dispersions of copolymers of 90 to 25 99.5% by weight of acrylates or methacrylates of alkanols containing 1 to 4 carbon atoms and 0.5 to 10% by weight, based in each case on the copolymer, of hydroxyalkyl acrylates and methacrylates having 2 to 20 carbon atoms in the hydroxyalkyl radical, such as hydroxyethyl, hydroxypropyl or hydroxybutyl acrylate or methacrylate. Such dispersions are known per se and can be prepared conventionally by emulsion polymerization (see Houben-Weyl, Methoden der organischen Chemie, 4th edition, vol. E 20, p. 217 ff.).

35 Suitable aqueous polyurethane dispersions are those of the type known per se, as described in, for example, US-A 3,479,310, GB-A 1,076,688, US-A 4,108,814, US-A 4,092,286, DE-A 2 651 505, US-A 4,190,566, DE-A 2 732 131 or DE-A 2 811 148.

40 The aqueous dispersions used may comprise the customary auxiliaries and additives. These include, for example, fillers, such as quartz powder, quartz sand, highly dispersed silica, heavy spar, calcium carbonate, chalk, dolomite or talc, which are often used together with suitable wetting agents such as 45 polyphosphates, for example, such as sodium hexametaphosphate, naphthalenesulfonic acid, ammonium or sodium salts of polyacrylic

acids, the wetting agents being added generally in amounts of from 0.2 to 0.6% by weight, based on filler.

Further suitable auxiliaries are organic thickeners to be used in amounts, for example, of from 0.01 to 1% by weight, based on the dispersion, such as cellulose derivatives, alginates, starch or starch derivatives or polyacrylic acid, or inorganic thickeners to be used in amounts of from 0.05 to 5% by weight, based on the dispersion, such as bentonites, for example.

10 Fungicides for preservation may also be added to the dispersions. These are employed generally in amounts of from 0.02 to 1% by weight, based on the dispersion. Examples of suitable fungicides are phenol and cresol derivatives and also organotin compounds.

15 Substrates for impregnation are, for example, synthetic or nonsynthetic fibers and/or woven or nonwoven fabrics comprising such fibers.

20 The mixtures of the invention can be dispersed very finely in aqueous dispersions. The resulting dispersions are very stable on storage. Moreover, little of the water-emulsifiable polyisocyanate need be added in order to set the desired properties of the dispersion or to achieve the desired properties 25 during application.

The mixtures of the invention can of course be provided with customary auxiliaries and additives of coatings technology. These include, for example, defoamers, thickeners, leveling assistants, 30 pigments, emulsifiers, dispersing assistants, and also solvents. The desired processing viscosity is set by adding water.

To prepare the dispersions it is sufficient in the majority of cases to use simple emulsifying techniques, for example, with a 35 mechanical stirrer, or else in many cases simple mixing of the two components by hand, in order to obtain dispersions having very good properties. Naturally it is also possible, however, to employ mixing techniques involving a relatively high shearing energy, such as jet dispersion, for example.

40 The coating materials comprising the mixtures of the invention may be used in particular as primers, surfacers, pigmented topcoat materials, and clearcoat materials in the sector of automotive refinish or the painting of large-size vehicles. The 45 coating materials are particularly suitable for applications where particularly high application reliability, outdoor weathering stability, optical properties, solvent resistance,

chemical resistance, and water resistance are required, such as in automotive refinishing and the painting of large-size vehicles.

- 5 The coating materials comprising the mixtures of the invention may be applied by any of a wide variety of spraying methods, such as, for example, air-pressure, airless or electrostatic spraying methods using one-component or two-component spraying units, or else by spraying, troweling, knife coating, brushing, rolling,
10 roller coating, flow coating, laminating, in-mold coating or coextrusion.

The coatings are generally dried and cured under normal temperature conditions, i.e., without heating the coating.

- 15 Alternatively, the mixtures of the invention may be used to produce coatings which following application are dried and cured at elevated temperature, e.g., at 40 - 250°C, preferably 40 - 150°C, and especially from 40 to 100°C.

- 20 Despite the fact that certain publications relating to the preparation of water-emulsifiable polyisocyanates, such as DE-A1 40 01 783, EP-A2 206 059, EP-A2 486 881, EP-A1 540 985 or DE-A1 199 58 170, include mixtures of isocyanurates and/or biurets of 1,6-diisocyanatohexane (HDI) and isocyanurates of
25 1-isocyanato-3,5,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI) with emulsifiers within long lists of suitable starting isocyanates, it was impossible for the skilled worker to infer from any of the abovementioned publications any specific indication whatsoever that the mixtures according to the
30 invention exhibit improved hardness, an improved increase in hardness, and a ready emulsifiability at the same time. Moreover, as compared with the prior art, the mixtures according to the invention exhibit a longer "potlife", this being the period of time within which a batch remains usable after all of the
35 constituents have been mixed, and does not, for example, undergo separation or premature curing.

The examples which follow are intended to illustrate the properties of the invention but without restricting it.

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Examples

In this specification, unless indicated otherwise, parts are to be understood as meaning parts by weight.

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Tests

All specimens were tested in the formulation given below:

Binder dispersion

- 5 240 p Daotan® 1225 (from Solutia)
- 119 p Plusaqua® V 608 (from Omya)
- 310 p distilled water
- 18 p Fluorad® FC 430 (from 3M)
- 9 p AMP 90 (from Angus Chemie)

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One part of the polyisocyanate was added with stirring to one part of this binder dispersion (amounts relate to nonvolatile weight fractions).

- 15 The finished emulsion was applied with a 200 µm doctor blade to a degreased metal panel and was flashed off at room temperature for 20 minutes before the painted panel was baked in a gradient oven for 30 minutes. Prior to testing, the finished panels were stored for 24 hours under standard conditions (50% humidity, 23°C). The
- 20 hardness of the paint films was then measured by means of a pendulum damping test in accordance with DIN 53157 (König hardness). Measurements are indicated in pendulum swings (the higher the number of pendulum swings, the harder the paint film).

25 Isocyanate A1:

HDI isocyanurate having an NCO content of 22.2% and a viscosity at 23°C of 2.8 Pas

30 Isocyanate B:

IPDI isocyanurate having an NCO content of 17.2% (Vestanat® T 1890/100 from Degussa)

35 Abbreviations:

- HDI hexamethylene diisocyanate
- IPDI isophorone diisocyanate
- PC propylene carbonate

40 T parts by weight

Example 1 - Hydrophilized isocyanate = polyisocyanate a1

26 g (0.146 mol) of a mixture of 80 parts 2,4-tolylene diisocyanate and 20 parts 2,6-tolylene diisocyanate were added to 45 150 g (0.30 mol) of a monofunctional polyethylene oxide with an OH number of 112, prepared starting from methanol, at 60°C and the mixture was stirred for 60 minutes (= c2). The emulsifier thus

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obtained was cooled to 30°C and 900 g of isocyanate A1 were stirred in. This gives a water-emulsifiable polyisocyanate (= a1) having an NCO content of 18.4% and a viscosity at 23°C of 3.0 Pas.

5 Isocyanate a1, isocyanat B, and propylene carbonate were mixed in the proportions indicated in the table.

10	Example No. 1	Isocyanate a1 (g)	Isocyanate B (g)	PC (g)	NCO content (%)
1	28	5	22	10.9	
2	24.5	7.5	21.33	10.8	
3	21	10	20.67	10.8	
4	17.5	12.5	20	10.7	
15	Comparative, C	30	./.	20	11.0

Results: example 1

20	Baking temp. [°C]	Pendulum damping				V
		1	2	3	4	
60	44	41	43	52	26	
70	67	68	64	74	36	
80	93	87	107	105	42	
90	98	108	122	124	45	
100	121	126	126	136	47	
110	125	128	130	138	53	
120	126	131	131	140	94	
130	126	132	132	141	99	
140	126	132	136	141	99	
150	130	132	138	141	101	

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Example 2

solvent-containing hydrophilicized isocyanate B = isocyanate b1

35 14 g (0.014 mol) of a monofunctional polyethylene oxide of molecular mass of 1 000, prepared starting from methanol, are added to a solution of 125 g (0.51 eq NCO) of isocyanate B in 53.6 g of Solvesso® 100 (about 28% by weight). The mixture is stirred at 85°C for 3 hours and, after cooling, gives a turbid, 40 viscous paste having an NCO content of 11% (= b1), which with considerable mechanical effort can be converted into an aqueous, coarse emulsion.

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By preparing mixtures of hydrophilicized isocyanate b1 and of the hydrophilicized isocyanate a1 described in example 1, with the addition of propylene carbonate, a readily emulsifiable isocyanate mixture is obtained which results in a fine emulsion.

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	Example No. 2	Isocyanate a1 (% by weight)	Isocyanate b1 (% by weight)	PC (% by weight)	NCO content (%)
10	1	56	24	20	12.9
	2	60	20	20	12.9
	3	68	12	20	13.1
	4	76	4	20	13.4
15	Comparative, C	80	-	20	13.5

Results example No. 2

20	Baking temp. [°C]	Pendulum damping				
		1	2	3	4	C
	60	37	29	21	27	19
	70	64	58	48	51	40
25	80	76	88	72	78	59
	90	94	109	87	89	76
	100	99	114	95	91	85
	110	105	119	96	92	86
	120	108	122	99	97	85

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